

## ***Interactive comment on “Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign” by T. M. Butler et al.***

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We fundamentally agree with the sentiments expressed by Karl et al (2008) in their interactive comment, that current understanding of the chemistry of isoprene oxidation and mixing processes in the planetary boundary layer (PBL) is at a very primitive stage, and that much remains to be learned, for example through the interpretation of field observations.

Karl et al (2008) claim that our hypothesis, that the intensity of segregation between isoprene and OH in the PBL could be as high as 50%, is "rationalized based on work by Krol et al (2000) and Verver et al (2000)". We prefer to take the view that our work is

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based soundly on interpretation of the unique set of observations obtained during the GABRIEL airborne field campaign. We make a compelling case in Butler et al (2008) that some degree of segregation is essential in order to explain the observations of bulk OH and isoprene mixing ratios observed simultaneously in the PBL over Suriname in October 2005, given the degree of certainty associated with laboratory measurements of the isoprene + OH rate constant. Previous work is cited as support that segregation effects have previously been recognised as potentially important in the PBL.

Karl et al (2008) make a couple of very good points regarding the chemistry of isoprene oxidation. It is true that if OH were to be recycled through reaction of first generation isoprene-derived RO<sub>2</sub> with HO<sub>2</sub>, that this may tend to lower the intensity of segregation between isoprene and OH. In Butler et al (2008), we do not actually suggest that OH is recycled in this way. In our conclusions we make it clear that it is beyond the scope of our present work to speculate on the true origin of the OH recycling which is clearly required to explain the GABRIEL measurements. Isoprene oxidation is a very complex process involving many intermediate species. Exactly which of these intermediates is involved in OH recycling is the subject of ongoing theoretical and laboratory work. Determining the effect of this OH recycling on the intensity of segregation will require detailed knowledge of the chemical and mixing timescales involved, and would certainly benefit from work with LES models.

Karl et al (2008) also suggest that model studies of the intensity of segregation can be influenced by the complexity of the chemical reaction scheme used. We do not see why this should necessarily be so. We look forward to published work examining this in more detail. For now we note that the chemical reaction scheme used in our model contains 278 reactions of 132 species, is thus amongst the most complex of chemical mechanisms ever to be used in a global three dimensional model, and is second only to the Master Chemical Mechanism in the complexity of its treatment of isoprene oxidation.

Karl et al (2008) state, quite correctly, that (in a model) "a well- mixed grid cell average

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would underestimate the true variability (and possible segregation) of reactants occurring in the real atmosphere". Naturally, we agree completely with this statement. Karl et al (2008) point to their own 2007 work which indirectly shows that isoprene and OH may be segregated in cloud layers. It is possible to hypothesise many more mechanisms by which reactants may be segregated in the PBL. In Butler et al (2008) we suggest three: dry convective plumes; a heterogeneously distributed canopy flux; and possible scavenging of OH by co-location of isoprene with other more reactive compounds. The global three dimensional model employed is not capable of resolving this segregation, but we have inferred its effect by comparison of our simulated results with the GABRIEL measurements. The strength of our global modelling approach is in our ability to perform sensitivity studies at the global scale, which we report in Butler et al (2008).

Finally, we agree with Karl et al (2008) on the central role which field measurements have to play in improving our understanding of isoprene oxidation in the atmosphere. We have made use of the unique set of measurements taken during the GABRIEL airborne field campaign and determined the degree of OH recycling and isoprene-OH segregation required in our model in order to achieve agreement with these measurements. Other workers with LES models at their disposal will use similar field data to study the segregation in more detail. We also reiterate that theoretical and laboratory work has an important role to play in advancing our understanding of isoprene oxidation in the atmosphere.

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